AD-A268 931

FINAL REPORT

PROGRAMME, SUMMARY AND ABSTRACTS
DISCUSSION MEETING.

AGEING IN PROCESSED POLYMERS

UNIVERSITY OF BIRMINGHAM

5-7 MAY 1993

DTIC
ELECTE
SEP 07 1993
A

SPONSORED BY THE

UNITED STATES OFFICE OF NAVAL
RESEARCH EUROPE

AND THE

UNITED STATES AIR FORCE
EUROPEAN OFFICE OF AEROSPACE
RESEARCH AND DEVELOPMENT
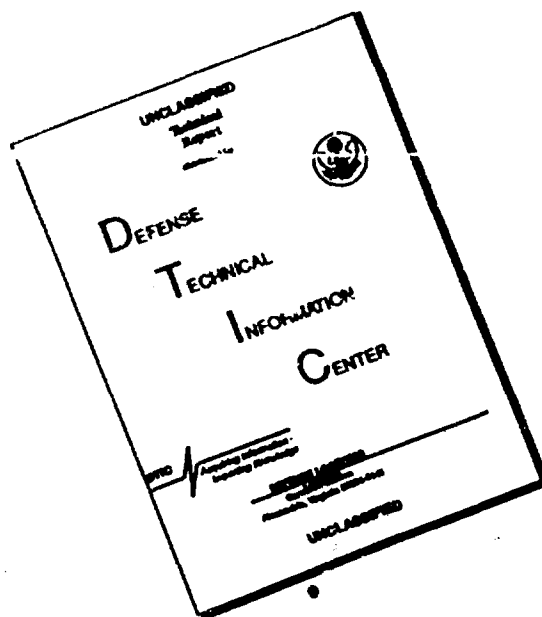
Conference Organisation:

Dr M J Richardson
National Physical Laboratory
Teddington
Middlesex TW11 OLW

Phone: 081 943 6785
Fax: 081 943 6755

Professor J H Magill
Office of Naval Research
223/231 Old Marylebone Road
London NW1 5TH

Phone: 071 409 4131
Fax: 071 723 1837

DISCLAIMER NOTICE

THIS DOCUMENT IS BEST QUALITY AVAILABLE. THE COPY FURNISHED TO DTIC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

TABLE OF CONTENTS

93   9   02   130

93-20664

PROGRAMME

Wednesday 5 May

13.55	Introduction and Welcome
14.00	Enthalpic Ageing in Polymers: Structure/Property Relationships and Some Unresolved Questions R Ferguson (Dept of Chemistry, Heriot-Watt)
14.45	Ageing of Starch-Based Products below the Glass Temperature S Livings (Cavendish Laboratory, Cambridge)
15.30	Tea
16.00	Enthalpy Relaxation and Physical Ageing in Polymers J M Hutchinson and U Kriesten (Dept of Engineering, Aberdeen)
16.45	The Effect of Ageing on the Material Properties of Polymer Glasses J N Hay (Dept of Chemistry, Birmingham)

Thursday 6 May

09.00	Structure and Relaxation in Glassy Polycarbonate T Pakula (Max-Planck-Institut, Mainz)
09.45	Thermal and Mechanical History-Dependent Properties of Polymers in the Glassy State J Perez (INSA, Villeurbanne)
10.30	Coffee
11.00	Crystallisation Phenomena in Glassy Polymers as Revealed by Real Time Dielectric Spectroscopy T A Ezquerra and F J Balta Calleja (CSIC, Madrid)
11.45	Physical Ageing of Polymers Studied by DMTA and DETA Techniques R E Wetton (Polymer Laboratories, Loughborough)
12.30	Lunch

14.00	Investigation of Physical Ageing in Polymers by Positron Annihilation Spectroscopy W J Davies and R A Pethrick (Pure & Applied Chemistry, Strathclyde)
14.45	Coupling Model Approach to Linear and Non-Linear Relaxations in Polymers K L Ngai (Naval Research Laboratory, Washington)
15.30	Tea
16.00	Modelling of Creep and Physical Ageing in Thermoplastics B E Read, G D Dean and P E Tomlins (NPL, Teddington)
16.45	Prediction of Effects of Physical Ageing on Long-Term Mechanical Properties by Finite Element Methods K C McEwan, T G F Gray and W M Banks (Mechanical Engineering, Strathclyde)

Friday 7 May

09.00	Several Aspects of Ageing in Glassy and Plastically Deformed Glassy Polymers E F Oleinik (Institute of Chemical Physics, Moscow)
09.45	Sequential Ageing Theory: Comparison of the Model with Experiment N G McCrum (Engineering Science, Oxford)
10.30	Interpretation of Mechanically-Induced Ageing and De-Ageing in Terms of Redistributing Internal Stress C P Buckley*, P J Dooling[+] and S Hinduja[+] (*Engineering Science, Oxford and [+]Mechanical Engineering, UMIST)
11.00	Coffee and General Discussion and Evaluation
12.30	Lunch

SUMMARY

The manufacture of almost any plastic article involves some form of quenching as occurs, for example, in extrusion or injection moulding. The primary intention is to extract the product from, say, a mould as quickly as possible in order to maximise productivity. This, unfortunately, cannot be equated with the structural stability of the workpiece and so the properties of the formed component may subsequently change (ie age) as it slowly relaxes to a more stable state. Such a process is purely physical in origin and may be reversed on heating: it must be distinguished from the more familiar chemical effects which are generally irreversible and are associated with decreases in molar mass.

"Physical ageing" was not a serious problem when polymers were used only for low grade applications (although even here it contributed to the "cheap and nasty" image that is still widespread for plastics - a simple example is the warping of an article that was well formed initially). Now that plastic components are increasingly *designed* for use in demanding situations it becomes essential for the manufacturer to have the ability to forecast long-term changes (particularly in the dimensional, mechanical and thermal properties of the processed component). This, in turn, implies the existence of simple and rapid tests that are able to define the condition of an aged component at some time after its fabrication.

This Discussion Meeting was intended (i) to survey our present knowledge, (ii) to identify common features in the various manifestations of physical ageing and (iii) to indicate outstanding problems - and plausible routes to their solution. Lectures considered:

1   specific techniques that are used to characterise ageing

2   the relationships of these to ultimate properties

3   empirical and fundamental models

4   the predictive validity of such models.

One of the commonest techniques used to study ageing in polymers is differential scanning calorimetry (DSC) because of the ease of sample preparation and the simple experimental

procedure. An extensive body of DSC "relaxation" information is now available for polymers and blends and it is becoming feasible to discuss "structure (repeat units) - property" relationships in a meaningful manner, although we are still some way away from real predictive capability in this respect. One definite advance for binary blends with widely separated T_g's is that ageing is dominated by the component with lower T_g. There is still controversy over the equilibrium enthalpy limit to which a glass can relax - is it given by a simple extrapolation of the supercooled liquid or is the non-linearity of the enthalpy-temperature curve greater then is implied by a linear C_p-T curve? The latter is suggested by the results when this quantity is considered as another unknown but this approach does *not* seem to be validated for the few cases when the extrapolation can be made using data obtained for oligomers.

At the other experimental extreme from DSC as a technique is positron annihilation spectroscopy (PAS) which gives information on the free volume (V_f) - both the average value and its distribution - in a system. V_f is a key parameter in many theories of ageing and the complexity of the PAS procedure will only be fully justified if V_f can be unambiguously defined as a function of mechanical and thermal history.

Although DSC and specific volume (density) measurements undoubtedly reflect the effects of physical ageing, it is not clear how the observed changes are related to those parameter measurements of more immediate practical value - the several mechanical moduli or yield stresses, for example. There was general agreement at the Workshop that the changes in thermodynamic properties correlate with the increases in the elastic modulus and the tensile, flexural and compression yield stresses (which, in turn, imply decreased impact strengths, fracture toughness and ultimate elongation - ie increased brittleness). By contrast, creep data correlate only with changes in specific volume and not with DSC results. In this instance creep and specific volume are found to relax much more rapidly than enthalpy. The point is emphasised by data obtained for polycarbonate at room temperature; this polymer is stable with respect to enthalpy (on time scales of up to 15 years) whereas the creep compliance and density change for several days after quenching the sample. At the meeting there was a widespread (but mixed) feeling that samples are "deaged" by stress (due to the regeneration of free volume) so that at some yield limit much of the sample history may be eliminated and consequently correlations between thermodynamic and mechanical behaviour may be somewhat fortuitous. It seems highly likely that direct 1:1 relationships between properties are the exception rather than the rule. Different experimental techniques are likely to sample different regions of the overall relaxation spectrum that are influenced by the summation of

imposed restraints experienced during the history of a sample. Even the thermodynamic quantities, density and enthalpy, which normally change in parallel with each other under simple conditions, show divergent behaviour when stress is applied to the specimen.

Modelling of ageing behaviour was discussed from two very different points of view (i) the engineering and (ii) the molecular dynamics approaches. Ideally, the two should be comparable but this desirable situation is still not experienced. Creep models for engineering calculations, which incorporate ageing behaviour, are reasonably successful. They may use empirical functions that are not accepted universally but show the general form that is implied in a more basic analysis. In the latter category, several phenomenological models have had success in predicting/explaining such features as the fine structure of DSC curves in the vicinity of the T_g region. Unfortunately, the anticipated "structural parameters" that may be extracted from the measurements seem to have little basic meaning. The need for realistic microscopic models remains high and the promising approaches used by Ngai, Pakula, and Perez were discussed. These models must use independent molecular parameters in order to simulate the reasonable success of the empirical models. Only when this occurs will the problems of physical ageing be resolved meaningfully.

Enthalpic ageing in polymer glasses:
a) Structure property relationships, b) Some unresolved questions

Roderick Ferguson
Department of Chemistry, Heriot Watt University,
Edinburgh, Scotland

Differential scanning calorimetry has proved to be a simple and reliable technique for monitoring physical ageing processes in polymer glasses. Methods for analysing the Cp data obtained from such experiments fall into two general categories:- a) Cp curve shape analysis (eg the phenomenological multiparameter model of Hodge) or b) Enthalpy change as a function of ageing time and temperature (eg the empirical Cowie Ferguson model). We have concentrated on the latter methodology because:-

(i)   Thermal lag effects have more influence on the shapes of Cp curves than for enthalpy changes.

(ii)   The ageing parameters obtained from the phenomenological model vary both as a function of ageing time and temperature and hence have limited use in a predictive sense.

(iii)   Although the phenomenological models can fit Cp curves quite well, the corresponding enthalpy changes due to ageing are found to be at least 2-3 times bigger than those found experimentally.

(iv)   Enthalpy changes due to ageing can be correlated with volume relaxation experiments.

Enthalpic ageing data have now been obtained for a range of homopolymers, some copolymers and several blend systems, so that one can start to consider the dependence of the enthalpic ageing parameters on the chemical structure of the polymer repeat unit(s) ie structure property relationships.

Two useful parameters that can be obtained from the Cowie/Ferguson model parameters (log t_c and β) are the time to reach 99.9% of thermodynamic equilibrium, t_e and the average segmental activation energy, $<E_a>$. This latter quantity is related to the relaxation time distribution function, $\rho(\tau)$, which in turn can be obtained from the relaxation function, $\phi(t_a)$. Values of $<E_a>$ obtained at an ageing temperature of Ta = Tg-10 K are of the same order of magnitude as the activation energy requirements for processes such as the mechanical β relaxation in PMMA. Furthermore, there is a strong linear correlation between $<E_a>$ and the enthalpic Tg. Values of Log(t_c) obtained at Ta = Tg-10K also exhibit a reasonable linear correlation with Tg.

For a range of SAN copolymers, the CF model ageing parameters were found to vary with copolymer composition. For blends where the Tg's of the two components are not too far apart, the ageing parameters were found to exhibit a weak dependence on the copolymer composition. However, in blends where the two component Tg's are far apart (such as PVME and PS), the physical ageing is found to be dominated by the more mobile lower Tg component.

There still remain several unresolved questions in the field of enthalpic ageing in polymer glasses, namely:-

1a)   Is it valid to obtain the equilibrium enthalpy change for an infinitely aged sample, $\Delta T_\infty(T_a)$, from a simple extrapolation of the liquid enthalpy data ? (as has been assumed by many workers in this field).

1b)   Does the presence of topological constraints in the polymer glass mean that $\Delta H_\infty(T_a)$ will always be smaller than expected ?

2)   How can the phenomenological multiparameter model(s) be improved so that a) the parameters obtained from them do not vary with ageing time or temperature and b) these models successfully predict the observed enthalpy changes ?

Ageing of Starch-Based Products Below the Glass Transition

Simon Livings
Cavendish Laboratory, Madingley Road, Cambridge CB3 OHE

Starch is formed via the process of photosynthesis and is used as the energy reserve for plants. It is comprised predominately of two α-glucans, amylose which is essentially linear and amylopectin which is highly branched. On cooking starch in the presence of water, the structure becomes disrupted and the system forms a gel. On storing the gel (moisture content 20-80%) at temperatures above the glass transition, the amylopectin chains form a double helix. This reordering process is known as 'retrogradation' and is the basis for the mechanism of why bread goes stale. However low moisture starch systems (<20%) have their Tg above room temperature thus retrogradation does not occur during normal storage conditions.

When starch wafers (<20%) are annealed at temperatures below the glass transition an endothermic peak, as measured by differential scanning calorimetry (DSC) is found to occur below the glass transition. The peak position and enthalpy of this peak is found to be a function of both the annealing time and temperature. At long annealing times and sufficiently high temperatures the endothermic peak superimposes on the sigmoidal glass transition curve to give the well known glass transition overshoot. WAXS studies on wafers have shown the appearance of a peak at $2G°$ 2θ on ageing. This peak position is consistent with a starch molecule forming a single helix. NMR studies by Gidley et al [1] have shown that as the amount of ageing increases the proportion of starch in the single helix conformation also increases. FTIR has shown a conformational change of the starch molecules during ageing. The phenomenological changes that occur below Tg can be attributed to the process of enthalpy relaxation, favouring this specific ordering process.

For an ordered structure to be formed during annealing in the glassy state, one would expect the Narayanaswamy parameter x to have a comparatively low value. Using the peak shift method of Hutchinson et al [2] the Narayanaswamy parameter x for starch has been calculated and has been found to be invariant of the annealing temperature, this is consistent with the KAHR theory. The low value of x ~ 0.28 is compatible with the ability of starch to form a single helical structure below Tg and can be compared to PVC which has a low x value (0.26) and forms an x-ray peak below Tg. Using a non-linear least squares fit to the enthalpy versus time data (Cowie and Ferguson [3]) the β nonexponential factor has also been found for the various annealing temperatures.

REFERENCES

1. A.M. Appelqvist, D. Cooke, M.J. Gidley, S.J. Lane. Preprint Carbohydrate Polymers. Thermal properties of polysaccharides at low moisture 1. An endothermic melting process and water carbohydrate interactions.

2. J.M. Hutchinson, M. Ruddy. Journal of Polymer Science. Part B: Polymer Physics. 26, 1988, 2341-2366.

3. J.M.G. Cowie, R. Ferguson. Macromolecules. 22, 1989, 2307-2312.

Enthalpy Relaxation and Physical Ageing in Polymers

J M Hutchinson and U Kriesten
Department of Engineering, Aberdeen University,
King's College, Aberdeen AB9 2UE

The phenomena of enthalpy relaxation in glasses in general (and in polymer glasses in particular) and of physical ageing in polymers are both well documented. The former is a direct result of structural changes which occur on annealing a glass below the glass transition temperature Tg; the latter here refers to changes in mechanical properties which result from this annealing, and which are usually presumed to be dependent upon these structural changes. The details, and particularly the quantitative aspects, of the relationship between these two phenomena are not clear, however. Furthermore, in semi-crystalline polymers this relationship appears to be significantly different from that in amorphous polymers. This paper addresses these points by reference to enthalpy and volume relaxation and to physical ageing in both polystyrene and polypropylene.

Polystyrene has been investigated at 53 °C and at 89 °C, far below and just below Tg, respectively. Measurements of enthalpy recovery have been made by differential scanning calorimetry (DSC), and the usual behaviour is observed: on reheating in the DSC the endothermic response exhibits a peak at a temperature that increases with increasing annealing time. Enthalpy changes can be determined from these traces, and time-scale changes for structural relaxation can be evaluated on the basis of conventional models (eg Tool-Narayanaswamy).

Similarly, physical ageing has been studied by means of small strain torsional creep, and superposition of the creep data has been achieved using McCrum's method, which allows for changes in the limiting compliances on ageing. Double logarithmic shift rates very close to unity are found at both temperatures. These rates are much higher than the equivalent shift rates for enthalpy relaxation. The implication is that the mechancial relaxation time spectrum shifts much more rapidly on annealing than does the structural (enthalpy) relaxation time spectrum.

Further deviations from a simple relationship between the two spectra are noticed when the time-scales for equilibration near Tg are considered. After about 1000 hours, physical ageing at 89 °C appears to cease, whereas enthalpy relaxation continues over time-scales very much longer. In contrast, this is approximately the time required for volume relaxation to approach equilibrium, and it would therefore appear that volume relaxation is more closely related to physical ageing than is enthalpy relaxation.

Polypropylene has been studied at 19.5 °C by both DSC and physical ageing. Good superposition of creep curves can be obtained by a combination of horizontal and vertical shifting, giving a double logarithmic shift rate of 0.72, significantly less than the value of unity found for polystyrene. The relationship with the enthalpy relaxation process is much more complex here, as the ageing (annealing) temperature of 19.5 °C is above the nominal Tg around 0 °C.

The DSC traces on the annealed samples of polypropylene show the systematic growth of an endothermic peak at a temperature that increases with increasing annealing time. This is qualitatively the same behaviour as is observed for amorphous polymers, but here the effect apparently occurs above Tg. At the same time, the strength (ΔCp) of the relaxation at Tg appears to decrease on ageing.

The Effect of Ageing on the Material Properties of Polymer Glasses

J N Hay
The University of Birmingham B15 2TT, UK

It is now widely appreciated that glasses are not in thermal equilibrium with their environment but approach it over extended periods in a temperature region below but close to the glass transition temperature, Tg. Physical ageing is attributed to the progressive change in the glass towards equilibrium as a result of the restricted mobility of the chain segments as the temperature is reduced below the transition temperature and is associated with those molecular motions associated with the formation of the glass from the liquid on cooling. Consistent with these concepts, changes associated with physical ageing are reversible on heating above the ageing temperature.

As a result of physical ageing the material properties of the quenched glass change logarithmically with dwell time at the ageing temperature. The process has considerable commercial importance in that it is generally accompanied by what are perceived to be detrimental changes in mechanical and physical properties and changes which can occur in service, leading to variability in results and difficulties in comparing like polymers.

Thermal history is important, slower cooling rates in forming glasses and increased ageing times at lower temperatures increase the density of a polymer glass as well as its elastic modulus, tensile, flexural and compressive yield stresses. These in turn decrease the impact strength, fracture toughness and ultimate elongation, all generally considered to be associated with increased brittleness of the glass. In the case of many engineering polymers which fracture with a mixed mode mechanism, physical ageing leads to increased yield stress and this in turn reduces the contribution from shear yielding and can lead to brittle failure by propagation of a crack from a craze. The net effect is a progressive reduction in fracture toughness with extent of physical ageing.

Similar trends have been observed in compression and tensile stress-strain experiments in that the slip bands which develop on yielding become progressively more localised with the extent of physical ageing. There is also an increase in yield stress. In tensile experiments, the drop in load associated with the formation of the neck can release sufficient elastic energy, as heat, within the localised neck region to produce a thermal fracture of the specimen.

These trends in material properties outlined above correlate directly with the extent of physical ageing as measured by enthalpic relaxation, and density changes and so presumably are associated with segmental motion and the glass forming process. Other material property changes, however, do not correlate at all with the extent of enthalpic relaxation, in particular, changes in creep compliance. These have been widely used to follow the development of physical ageing and many developments in the kinetics of physical ageing are attributable to studies using this technique. Nevertheless, the creep compliance of quenched polycarbonate changes over dwell times of several days at room temperature, while samples of the material left at this temperature for 15 years do not exhibit enthalpic relaxation peak in their DSC traces. Measurement of physical ageing kinetics by DSC suggest that the process of enthalpic relaxation occurs in a temperature range limited to 50-70K below the glass transition temperature. If the overall retardation processes which account for the changes in the creep compliance with dwell time at room temperature have similar activation energies to that measured for segmental motion then in the higher temperature range

required for the enthalpic relaxation, they are associated with too short relaxation times to be attributable to enthalpic relaxation. Alternatively if they have relaxation times similar to those observed by DSC in the higher temperature range then the activation energies are not those normally associated with segmental motion of the molecular chains, ie the α-process.

This undoubtedly begs the question as to what is being measured by the various experimental techniques - are they measuring the same physical ageing process, are they equivalent and are they measuring the same spread of the overall relaxation processes which are present in a polymer glass?

Similar themes will be developed from dynamic mechanical, dielectric and IR spectroscopic as well as enthalpic relaxation studies on compatible and incompatible blends.

Structure and Relaxation in Glassy Polycarbonate

Tadeusz Pakula

Max-Planck-Institut für Polymerforschung, Postfach 3148, 6500 Mainz, Germany

Structural relaxation takes place in glass forming polymers during annealing below the glass transition temperature. It reflects in changes of many properties like volume, specific heat or mechanical properties. The extend of the relaxation depends on the structural state of the glass which can be influenced by processing conditions.

In this paper the relaxation of polycarbonate in the glassy state is studied by dilatometric, calorimetric and dynamic mechanical methods. The structure is characterised by X-ray scattering techniques. The influence of various sample treatments, including an isobaric or isochoric transition to the glass and the mechanical deformation, is considered.

The results support strongly the point of view that the structure of the glass has to be characterised by more than one order parameter. In the case of oriented samples the instability of properties is primarily related to the relaxation of internal stresses frozen in the material. A phenomenological model for description of these relaxations is presented.

Thermal and mechanical history dependent

properties of polymers in the glassy state

J Perez

Lab G.E.M.P.P.M. - u.a. CNRS 341
I.N.S.A. - Villeurbanne 69 621 - France

Glasses are known to undergo spontaneous densification during isothermal annealing. This volume recovery process, which is also an enthalpy recovery process can be viewed as the collapse of highly disordered sites or "quasi-point defects". We have modelled this physical ageing as a diffusion assisted annihilation of positive and negative defects. The diffusion mechanism is assumed to result from hierarchically constrained molecular mobility and the diffusion constant depends on the concentration of defects. Such a pattern helps us to describe the main features generally observed during physical ageing of polymers in their glassy state (Non-exponentiality, non-linearity, apparent activation energy).

Various experimental results are considered: for instance, a series of data obtained with PMMA and implying volume, enthalpy and dynamic modulus measurements, are discussed in accordance with this approach; more particularly, we have focussed our attention on low temperature annealing (about 100K below Tg) which shows that even in the β temperature range, the ageing effects mainly the low temperature tail of the α mechanical relaxation.

Since the well known results of Kovacs on memory effects observed with volume recovery experiments, there was a need for results allowing us to consider this memory effect as a general one: we succeeded in observing it with measurements of dynamic modulus in the case of polystyrene and, more recently, with measurements of enthalpy of PMMA and other glassy materials.

In agreement with the assumption of annihilation of defects during ageing, one can expect some rejuvenation effects from the creation of these defects: this can be provoked by low temperature plastic deformation of amorphous polymers. Some results obtained with polycarbonate, polymethyl-methacrylate and polyether-ether-ketone are presented. Thus the so-called "physical ageing" does not only result from thermal but also from mechanical treatments.

In conclusion, after having recalled the most known approaches given the literature in this field, a general frame is proposed in order to understand in a self-consistent way, the different aspects of time dependent thermal and mechanical properties of polymers in their glassy state.

Crystallization Phenomena in Glassy Polymers
as revealed by real time dielectric spectroscopy

T A Ezquerra, F J Baltá-Calleja

Instituto de Estructura de la Materia, C.S.I.C. Serrano 119,

Madrid 28006, Spain

The influence of crystallinity on the molecular dynamics of polymers shows novel aspects which can be investigated by dielectric spectroscopy. Segmental motions of the polymeric chain, appearing at temperatures above the glass transition temperature give rise to the α relaxation which is strongly affected by the presence of crystalline domains. Local motions like those causing the β relaxation are, on the other hand, less influenced by crystallinity.

The recent use of impedance analysers scanning over several decades in frequency within times lower than 1 minute allows one to perform dielectric measurements during crystallization in real time. In this communication we present dielectric relaxation measurements in real time performed in several polyesters including poly(ethylene terephthalate) and poly(ether ketone ketone) as crystallization proceeds from the glassy state. Data in the frequency domain are analysed in terms of the Havriliak Negami phenomenological model. Dipole moment time correlation functions have been calculated by pure imaginary Laplace transformation and then fitted to Kohlrausch-Williams-Watts functions. Results have been discussed in the light of different theoretical models.

Physical Ageing of Polymers Studied by DMTA
and DETA Techniques

R E Wetton

Polymer Laboratories Ltd, The Technology Centre,

Loughborough LE11 OQE

The glassy state is a non-equilibrium condition such that even volume and enthalpy values taken together will not uniquely describe it. This point will be illustrated with respect to poly(styrene) glasses formed under pressure.

A glass can be considered as a metastable state slowly relaxing with time towards an equilibrium condition defined by the extrapolation of the liquidus line. This is shown in Fig 1.

The physical changes accompanying the slow relaxation of the glassy state are termed physical ageing and can be completely reversed by reheating above Tg. The general effects of physical ageing in a wide variety of materials have been reviewed by Struijk [1]. In the present paper ageing in poly(styrene), epoxies and PVC are studied via changes in their dynamic moduli, damping and dielectric properties. An example of this is shown in Fig 2 and a general description of the methodology is given in reference [2]. The effect of continuous and discontinuous stress [3] during the ageing part of the experiment is reported by using the PL-Minimat in parallel experiments.

Dielectric measurements on PVC have been carried out on samples similar to those used in the mechanical experiments. A comparison of some of the data for a PVC sample quenched and then aged at 65 °C is given in Figure 3. Dielectric constant results do not exhibit as much change with ageing as dynamic moduli, because of the opposing effects of density increasing the concentration of dipoles but decreasing their extent of motion. Dielectric tan δ does, however, reflect the ageing process quite strongly and this could be an interesting area for remote sensing technology.

1   L.C.E. Struijk, Physical Ageing in Amorphous Polymers and other Materials, Elsevier, Amsterdam 1978.

2   R.E. Wetton, Developments in Polymer Characterisation 5 (Ed Dawkins) p 179.

3   B. Haider and J.L. Smith, Polymer 32 1991, 2594.
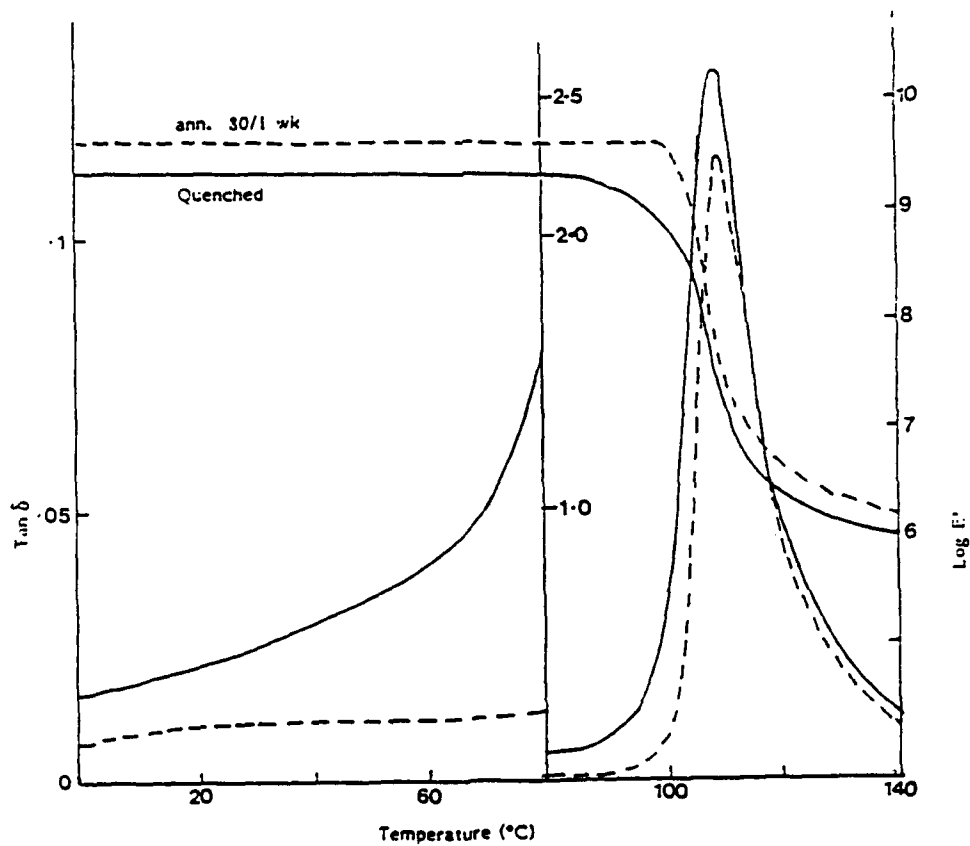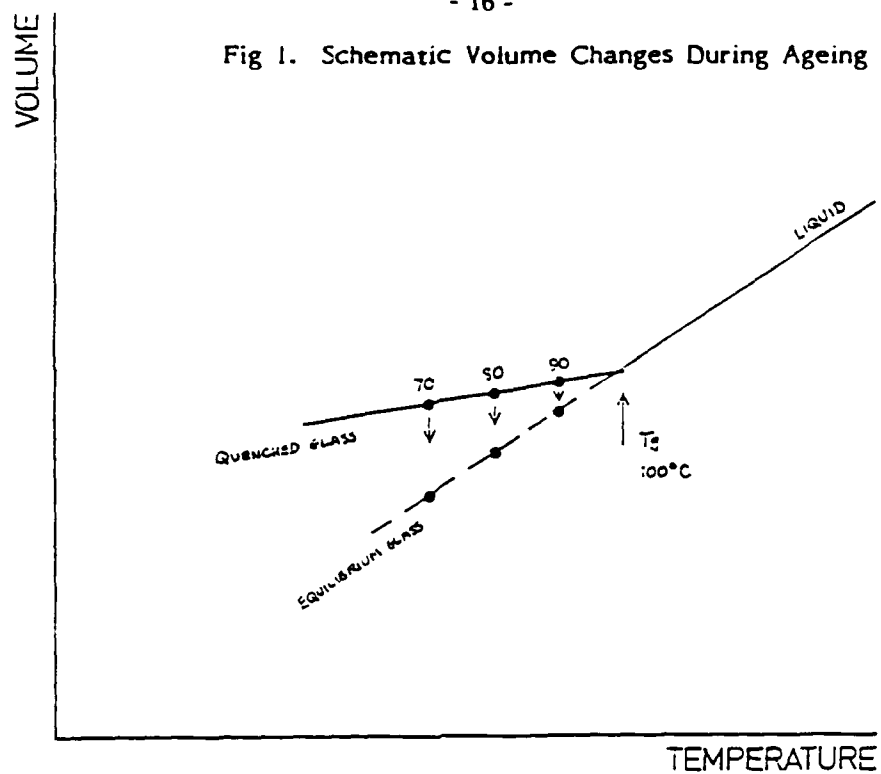
Fig 1. Schematic Volume Changes During Ageing

Fig 2. Effect of Ageing in the Dynamic Modulus
and loss in Poly(styrene)
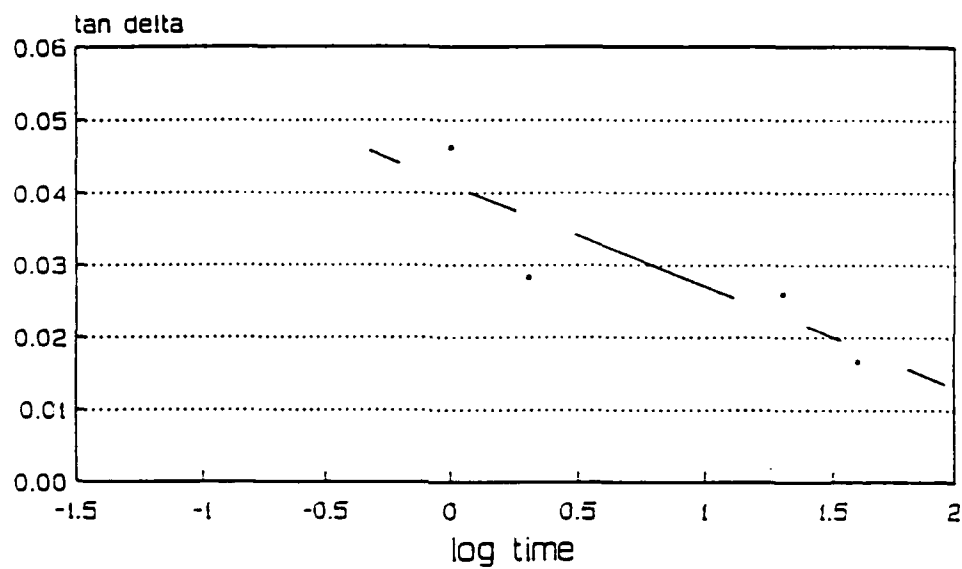
deta ageing
Tan δ_{D} at 65c

Fig 3. Changes in dielectric tan δ_{D} at 65°C for PVC after quenching

Investigation of Physical Ageing in Polymers by Positron Annihilation Spectroscopy

W J Davies, R A Pethrick
Department of Pure and Applied Chemistry
University of Strathclyde, Glasgow

Positron annihilation spectroscopy, (PAS), is used to measure free volume (V_f) in polymers. It is non-destructive, non-perturbing and gives a direct measure of the V_f distribution [1]. When positrons (e^+) enter a polymer system, they will interact with the electrons of that system and after some time period annihilate (mass is converted to energy) to form gamma-rays which can be detected. The occurrence in time, and the energy of these gammas depends on the electron density experienced by the e^- while in the polymer system. Measurement of the appropriate positron annihilation parameters will therefore yield information on the size and number of V_f holes present in the system.

PAS is a family of three experimental techniques. Positron annihilation lifetime spectroscopy (PALS), Doppler broadening spectroscopy (DBS) and angular correlation of annihilation radiation (ACAR). Each technique gives different information about the electronic environment experienced by the annihilating positrons.

Two state of the art PAS systems are currently being used, a high efficiency PALS spectrometer which is essentially a sophisticated timing instrument and measures the time each positron exists before annihilation (ca. 10^{-9} s). The DBS system incorporates a solid state hyper-pure coaxial Germanium detector which measures the precise energy of the annihilation photons.

Any polymer which contains an amorphous component and therefore free volume, will undergo a spontaneous time dependent process known as physical ageing when quenched from a temperature above the glass transition (Tg) to below it. Physical ageing involves a structural change in the material (structural relaxation) and manifests itself in changes in physical and mechanical properties. Molecular (segmental) mobility is reduced as the excess V_f in the system decays providing a more efficient packing of polymer chains.

Two approaches to measuring physical ageing have so far been used. Most straightforward is the direct measurement of a property that depends on the structural state of the material eg enthalpy or density. Alternatively the course of physical ageing can be monitored indirectly by assessing its effect on the mechanical relaxation of a polymer. This approach was used in the classic work carried out by Struik, who monitored the retardation of the mechanical creep behaviour of a wide range of materials [2]. Struik concluded that the unmeasured parameter giving rise to the observed changes in mechanical relaxation behaviour was V_f. Each momentary creep curve measured was proposed to represent the mechanical response of one structural state (one V_f distribution).

Any prediction of time dependent (viscoelastic) properties will therefore require understanding of the influence of excess V_f and its quantification.

Limited work by other authors [3-5] had shown that PALS could be used to monitor the isothermal changes in excess V_f that occur when a stepwise change in temperature provides a deviation from equilibrium state. It was proposed that this was a direct measurement of the V_f changes which can be measured by dilatometry, or whose influence is measurable by

determining the shift of momentary creep experiments. There is a requirement therefore to determine the correlation between the measured structural parameter ie V_f distribution, and its effect on the mechanical relaxation behaviour - thus allowing long-term mechanical relaxation behaviour to be determined from assessment of structure by short-term tests.

Isothermal relaxation experiments have been carried out on poly(methyl-methacrylate), Polystyrene and Polycarbonate. Most extensively studied so far is Polycarbonate, isothermal volume relaxation behaviour of which has been monitored at 30, 50 and 80 °C (after a rapid quench from about Tg). Isochronous thermal scans were also carried out on samples representing freshly quenched and near-equilibrium states to determine the difference in thermal response of their structural states.

Various fits were made to the isothermal relaxation data, including the Narayanaswany equilibrium density function (6). This model for structural relaxation describes the gradual (retarded) approach of the properties of a glassy polymer to their equilibrium values.

Many authors have shown that over long time ranges the ageing rate can be described as varying linearly with log time [2,5,7-9], this has been shown for volumetric, dynamic-mechanical, creep and positron data. However it has been shown that this type of fitting does not always adequately describe the behaviour of the materials investigated over the full time range measured. Analysis of polycarbonate data suggests that as ageing temperature decreases two distinct volume relaxation processes with different rates become detectable. This data can only be adequately described by means of two overlapping exponentials. The rate and extent of each process is determinable and is shown to vary as temperature is varied.

The Narayanaswany fitting procedure has also been shown to be inadequate in these instances since, although it allows for a distribution of relaxation times via the β exponent, it does not allow for a distribution of relaxation times composed of two major components.

REFERENCES

1.   D.M. Schrader, Y.C. Jean Eds, Positron and Positronium Chemistry, Elsevier Amsterdam 1988.

2.   L.C.E. Struik, Physical Ageing in Amorphous Polymers and Other Materials, Elsevier Amsterdam 1978.

3.   A.J. Hill, P.L. Jones, J.H. Lind, G.W. Pearsall, J. Polym. Sci: Part A, 26 (1988) 1541.

4.   A.J. Hill, I.M. Katz, P.L. Jones, Polym. Eng. Sci. 30 (1990) 762.

5.   Y. Kobayashi, W. Zheng, E.F. Meyer, J.D. McGervery, A.M. Jamieson, R.M. Simha, Macromolecules 22 (1989) 2302.

6.   G.W. Scherer, J. Amer. Ceramic Soc 69 (1986) C206.

7.   U. Kriesten, J.M. Hutchinson, Polymer 33 (1992) 4875.

8.   J. Bartos, J. Muller, J.H. Wendorff, Polymer 31 (1990) 1678.

9.   R.A. Venditti, J.K. Gillham, J. Appl. Polym. Sci 45 (1992) 501 1501.

Coupling Model Approach to Linear
and Non-linear Relaxations in Polymers

K L Ngai

Naval Research Laboratory

Washington, D.C. 20375-5320 USA

Ageing in polymers is a nonlinear relaxation problem in which the structure (or fictive temperature) changes with time. This makes the problem much more difficult to treat than linear relaxation of polymer with a structure that is independent of time. Naturally nonlinear relaxation is related to linear relaxation because the latter has to be recaptured in the limit of small nonlinearity by the former. To ensure that a theory of nonlinear relaxation is reliable it must be built on top of a viable theory of linear relaxation of polymers. In this talk I shall first introduce the author's coupling model of relaxation in complex correlated systems which has been applied with success to local segmental motion in amorphous and even semi-crystalline polymers. A number of important experimental facts are cited and shown to be uniquely consistent with the predictions of the coupling model. The purpose of this first part of the talk is to establish the fact that the coupling model is most satisfactory in describing linear relaxations in polymers. In the second part, attention will be focussed on an extension of the coupling model in the linear regime to the nonlinear regime. The results obtained as well as the problems encountered will be discussed.

Modelling of Creep and Physical Ageing in Thermoplastics

B E Read, G D Dean and P E Tomlins
National Physical Laboratory
Teddington, Middlesex TW11 OLW

Empirical functions have been employed to analyse creep compliance curves for thermoplastics over wide time ranges as a function of age state, stress and temperature. The physical age of a specimen was characterised by the elapsed time t_e between cooling from an elevated temperature, at which the polymer structure is at equilibrium with respect to the α-retardation process, and the instant of load application. Temperatures of the creep measurements were such that the effective retardation times for the β- and α-processes were respectively short and long compared with t_e. Under these conditions, a small decrease was observed in the magnitude of the β-process with increasing age but the retardation time for this process was independent of t_e. For the α-process, it was concluded from analyses of data from long-term tests (when significant further ageing occurs during the creep) that ageing involves an increase in α-retardation time and that the retardation magnitude is unaffected.

Creep compliance values increase with the stress level when this exceeds about 3-6 MPa. At short creep times this non-linear behaviour is consistent with a reduction in the α-retardation time by elevated stresses and appears to involve a stress-induced deageing of the polymer. Subsequently the α-retardation time increases with creep time, implying that the physical ageing has been reactivated, but the rate of increase depends on the stress level. The long-term creep behaviour can be accurately described by a stretched exponential function containing an effective α-retardation time that is related to t_e, creep time, stress and temperature. An application of the model will be illustrated with reference to data obtained for PVC.

Prediction of the Effects of Physical Ageing on Long Term
Mechanical Properties by Finite Element Analysis

K McEwan, T G F Gray, W M Banks

Department of Mechanical Engineering

Division of Materials

University of Strathclyde, Glasgow

Struik [1] demonstrated the significance of physical ageing in the glassy, non-equilibrium state of a polymer below Tg. This work showed the importance of taking account of physical ageing in any determination of long term mechanical and physical properties especially in the computation of time dependent deformations.

While a wealth of ageing data has been generated using various experimental techniques showing the influence on the physical and mechanical properties of polymers [1-3], there has been little attempt to correlate the various property changes with changes in structural state. In fact, there is generally a discrepancy between the rates and extents of ageing measured by the various techniques.

Free volume (V_f) is a fundamental property as it defines the structural state and controls mobility. The mobility of a polymer determines the rate at which the molecules can rearrange to approach thermodynamic equilibrium (physical ageing). The use of positron annihilation spectroscopy (PAS) to measure the kinetics of changes of V_f should enable the fundamental structural changes to be correlated with the changes in mechanical properties.

The critical property for engineering considerations is creep/stress relaxation as this determines the dimensional stability of a component, this being the most likely mode of "failure" - in the sense of the component not meeting its specification, ie warping to cause vibration or leakage, rather than the classic failure of yield or fracture. To develop the physical ageing concept in an engineering application a suite of commercially available packages are utilised.

MOULDFLOW a finite volume programme is used to simulate the injection process and produce the internal stresses generated within a component. These are the stresses that cause time dependent dimensional instability. Mouldflow itself can predict the warpage of a component on mould ejection, based on the differential cooling and stress gradients.

The output from mouldflow is read into PATRAN, used as a pre/post processor in this application. Two files from mouldflow are used, a geometry which is read directly into patran and a stress file, a conversion routine has been written to map the stresses onto the nodes and elements of the geometry model.

From patran the file is inputted to ABAQUS, a finite element solver, before being read back into patran for analysis and display of results.

The required law for creep behaviour is entered as a Fortran subroutine within ABAQUS.

At present insufficient mechanical data have been generated to develop a correlation between free volume and mechanical properties. The simplified creep behaviours modelled so far are:-

i)   A stretched exponential, Kohlrausch-Williams-Watts function [4], generally used to describe short term behaviour, ie momentary creep curves (one V_f, one structural state).

ii)   An effective time law [5] that determines the modulus value at the real time by calculating an equivalent time for use with the momentary curves.

iii)   A stretched exponential [6] in which the mean retardation time for the creep process is expressed as a function of creep time.

The yield response of poly(methyl-methacrylate) is being investigated by a program of tensile tests. The parameters being varied are ageing temperature, ageing time, test temperature and crosshead speed. The results produced so far are for samples aged for different times at 80 °C and tested at room temperature over a range of crosshead speeds from 1 to 100 mm/min. The data available so far show the modulus and yield stress increasing initially but after a set time the yield stress decreases while the modulus remains at its elevated value. Further tests at different ageing and test temperature, 50 °C and R.T are required before any correlation with V_f can be established. The results are in contrast to other studies [7] that show the yield stress increasing with ageing time to a limiting value and master curves being produced. The yield response has not yet been incorporated into the finite element program as a law for its behaviour has not yet been developed.

REFERENCES

1.   L.C.E. Struik, Physical Ageing in Amorphous Polymers and Other Materials, Elsevier Amsterdam 1978.

2.   R.A. Venditti, J.K. Gillham, J. Appl. Polym. Sci., 45 (1992) 501 1501.

3.   A.J. Hill, I.M. Katz, P.L. Jones, Polym. Eng. Sci., 30 (1990) 762.

4.   G.W. Scherer, Non-Crystalline Solids, 123 (1990).

5.   L.C.E. Struik, Polymer 30 (1989) 799.

6.   P. Tomlins, The Influence of Physical Ageing and Temperature on the Tensile Creep of PVC, National Physical Laboratory, DMM h087.

7.   C. G'Sell, G.B. Mckenna, Polymer 33 (1992) 2103.

Several Aspects of Ageing in Glassy and Plastically
Deformed Glassy Polymers

E Oleink

Institute of Chemical Physics, Russian Academy of Sciences

Moscow, Russia

Several aspects of ageing phenomenon which did not receive yet enough attention in literature will be considered. The following questions will be touched upon:

1. Results of the simultaneous measurements of Enthalpy and Volume recovery near Tg in T-jump experiments. The energy changes for the creation (or the disappearance) of the unity of free volume in polymeric glass (PS). The peculiarities in the behaviour of ΔH and ΔV.

2. The existence of the large excess of ΔH in plastically deformed polymeric glasses. Non-voluminal nature of the excess. Structural and kinetic features of the "defects". Plastic Shear Transformations (PST), responsible for the energy excess in deformed polymers.

3. PSTs and ageing in glassy polymers; the changes of stress-strain behaviour, relaxation of enthalpy and residual strains, the nature of anelasticity in glassy polymers, molecular mobility in deformed polymers, the nature of excessive energy dissipation processes in glassy polymers during their deformation, the nature of the plastic deformation heat in polymer glasses.

4. The analysis of several models, related to ageing phenomenon; free volume diffusion model; stochastic model of elastic-plastic media; "critical number of contacts" model. Certain consequences of the models.

5. Computer simulations of structural relaxation and mobility in simple glasses. Consequences from the simulations.

Sequential Ageing Theory:

Comparison of the Model with Experiment

N G McCrum

Department of Engineering Science, University of Oxford,
Parks Road, Oxford OX1 3PJ

The viscoelastic parameters, whose change have been proposed to explain ageing, are as follows:

(A)   A movement of the viscoelastic retardation times to longer times.

(B)   A decrease in the strength of the relaxation (J_R-J_U), where J_R and J_U are the relaxed and unrelaxed compliances of the relaxation, respectively.

(C)   A decrease in J_U.

(D)   A decrease in the viscoelastic 'background'.

Of these, the two most dominant are (A) and (B), but it is entirely possible that all four make contributions to an ageing process. In this lecture I will confine attention to process (A); the term 'ageing' will be used to mean a small movement of viscoelastic retardation processes to longer times, with no change in strength. The author's intention is to illustrate in a simple manner the consequences of a sequential mechanism and this is done most easily by considering one mechanism alone. In the well-known ageing studies of Struik, following a quench, usually of up to 100 K, isothermal shifts of creep curves are observed, which are often identified with shifts of the viscoelastic spectra. These shifts can be large, for example 10^4 or 10^5. There is a clear paradox between this interpretation and received knowledge in the fields of Dynamic Mechanical Thermal Analysis and Dielectric Thermal Analysis,. which teaches that the temperature of a loss peak depends on the frequency of measurement, but not appreciably on thermal history of the specimen. The paradox is eliminated by the Sequential Theory of physical ageing. In a sequential model, the changes that cause ageing occur sequentially; that is, the retardation elements move to equilibrium with increasing ageing time (t_e) in an order which is determined by the retardation time: the shorter the retardation time the shorter the value of t_e at which equilibrium is achieved. The changes in the retardation spectrum, for example diminution in the magnitude of retardation elements or their shift to longer times, are small but because they occur in sequence they distort the spectrum sufficiently to generate the enormous shifts in the creep curves observed in a Struik plot. The curves of the Struik plot give the appearance of being superposable, but they do not in fact superpose exactly unless the equilibrium retardation spectrum is flat: in this unique case, exact superposition is possible and the shift parameter $\mu = 1.0$. The observation by Struik that μ increases with increasing temperature, reaching $\mu = 1.0$ at ~20 K below T_g, is attributed by the Sequential Ageing Theory to increasing temperature lowering the slope of the equilibrium spectrum.

Interpretation of Mechanically-Induced Ageing and De-ageing
in Terms of Re-distributing Internal Stress

C P Buckley*, P J Dooling[+] and S Hinduja[+]

*Department of Engineering Science, University of Oxford,

Parks Road, Oxford OX1 3PJ

[+]Department of Mechanical Engineering, UMIST

Manchester M60 1QD

A well-known nonlinear feature of polymer solid-state viscoelasticity is the apparent "de-ageing" followed by "re-ageing" that occurs under stress. If a stress σ_1 is applied at time t_1 and a stress σ_2 at time t_2 ($t_2 > t_1$), the strain $\varepsilon(t)$ resulting at time $t_2 + t$ from σ_2 increases with increasing σ_1 ("de-ageing"), but decreases with increasing elapsed time $t_2 - t_1$ ("re-ageing"). Similar behaviour is seen in stress relaxation. Such mechanically-induced ageing effects have been interpreted usually in terms of unknown structural changes caused by stress. One of us pointed out some time ago, however, that an alternative explanation is possible in view of the heterogeneity of polymers, in terms of a redistribution of microstress at some (as yet unspecified) level of a fixed microstructure [1]. We have recently returned to this question, in the course of developing a three-dimensional constitutive model for glassy polymers, for use in stress analysis. A form of model has been found that correctly exhibits a range of nonlinearities in polymer viscoelasticity. The material is modelled in three dimensions as being divided into viscoelastic zones that flow in shear according to Eyring kinetics but with varying free energy barriers. A natural consequence is the stress-induced "de-ageing" and "re-ageing" referred to above. In terms of the model, it occurs because of a re-distribution of three-dimensional stress between the zones. The model has been fitted quantitatively to PMMA, using data from torsion and combined tension/torsion creep tests, and has been used to simulate the apparent ageing phenomena.

[1]   C.P. Buckley, J. Phys. D: Appl. Phys., 10 (1977) 2135.